Comparative Studies of Poly(Dimethyl Siloxanes) Using Automated GPC-MALDI-TOF MS and On-Line GPC-ESI-TOF MS

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In this study we compare on-line gel permeation chromatography (GPC) electrospray ionization (ESI) time-of-flight (TOF) mass spectrometry (MS) to automated GPC matrix assisted laser desorption ionization (MALDI) TOF MS for poly (dimethylsiloxane) (PDMS) analysis. Average mass values for a hydroxyl-terminated PDMS (OH-PDMS) sample were obtained and compared to traditional GPC that was calibrated with narrow polystyrene standards, by direct ESI and MALDI MS analysis, by a summation of mass spectra of all GPC fractions, and also by the recalibration method determined by both mass spectrometric methods. Quantitatively, the difference noted here between these hyphenated techniques is that GPC-ESI-TOF MS effectively reports the low-mass oligomers and underestimates the high-mass oligomers, while GPC-MALDI-TOF MS effectively reports the high-mass oligomers and underestimates the low-mass oligomers. In the GPC-ESI-TOF MS experiments, ion current suppression was observed in the high molecular weight region. The suppression effect was confirmed by repeatable sample runs and by injecting different PDMS samples. Higher chromatographic resolution was observed for GPC-ESI-TOF MS compared to GPC-MALDI-TOF MS. In fact, truly mono-disperse oligomers were observed in the low molecular weight range from GPC-ESI MS experiments. (J Am Soc Mass Spectrom 2003, 14, 195–202) © 2003 American Society for Mass Spectrometry

The advent of soft ionization techniques such as matrix-assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) have provided chemists the ability to evaluate polymer samples with several different mass analyzers. Specifically for polysiloxane materials the information rich data obtained from such analysis has been used qualitatively for repeat unit and end group determination [1–7] and quantitatively for relative concentration [8, 9] and average mass determination [10, 11].

Several reviews appear in the literature that highlight many of the applications of polymer mass spectrometry analysis [12–15]. The general consensus for determining average mass values is that the accuracy of such measurements is limited to polymer samples having a relatively narrow polydispersity (PD) index of less than 1.2 [16–20]. Mass discrimination occurs with more broadly dispersed polymer samples such that the high molecular weight oligomers within the molecular weight distribution (MWD) are under-represented or not observed at all. Several reports have been written that hypothesize of the root cause for these discrimination effects [21–28].

One strategy to overcome these mass discrimination effects is to incorporate gel permeation chromatography (GPC) prior to mass spectrometry. GPC separates molecules based on their hydrodynamic volumes where large molecules elute from the column before the smaller molecules [29, 30]. With the GPC-MS combination the complexity of a broad MWD is minimized by independently evaluating nearly mono-disperse chromatographic fractions. This mass fraction data can be used to recalibrate the GPC trace to obtain absolute average mass values. Additionally, the MWD can be reconstructed by summing the mass fraction data from which average mass values can be computed. Several research groups have illustrated the powerful combination of GPC with MALDI and ESI MS for polymer analysis. In the most traditional sense, GPC can be incorporated by manually collecting GPC fractions in a number of vials for subsequent analysis by ESI [23, 31] or MALDI MS [5, 6, 10, 11, 23, 32–36]. This approach is relatively time consuming and very tedious since each collected GPC mass fraction requires sample preparation prior to MS analysis. Alternatively, GPC can be combined with ESI or MALDI MS in a more automated approach. For example, the solution infusion characteristics of GPC and ESI allow these techniques to be combined on-line [37–40]. Fei and Murray [41] have reported on-line GPC coupling to a MALDI source. However, to date most GPC-MALDI analysis employs

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deposition of the GPC effluent onto a MALDI sample target followed by mass analysis [42–49]. This method is not considered to be true on-line hyphenation, when compared to GPC-ESI MS, since the deposition of GPC effluent and subsequent mass analysis occurs in two discrete time events. Rather, within this context it is considered to be automated GPC-MALDI MS.

In this study we compare on-line GPC-ESI MS to automated GPC-MALDI MS for polymer analysis and as such it seems proper to use the polymer's average mass values obtained by traditional GPC analysis. Although traditional GPC provides *polystyrene-equivalent* average molecular weights, it remains useful as a benchmark in this comparative study.

Experimental

Poly(Dimethyl Siloxane) Materials and Chemicals

The three PDMS polymers with different end groups that include OH-PDMS, methyl-terminated (ME-PDMS), and α,ω-bis(4-hydroxylbutyl)-terminated (HB-PDMS) were synthesized in-house from previously described procedures [48]. Sodium nitrate and dithranol were obtained from Aldrich (Milwaukee, WI). HPLC grade tetrahydrofuran (THF) and isopropanol (IPA) were all purchased from Fisher Scientific (Fairlawn, NJ).

Gel Permeation Chromatography

The solvent delivery system used a Waters Alliance 2690 Separation Module (Waters Corporation, Milford, MA). All samples were prepared in THF at a concentration of 0.12% (wt/vol). The separation was performed on a set of two PL-gel mixed-E columns that were purchased from Polymer Laboratories, Amherst, MA. The dimension of the columns were 300 mm $\times$ 7.8 mm and the particle size of the packing materials was 3 μm. Fifty mL of the sample solution were injected into the GPC system. HPLC grade tetrahydrofuran was used as the mobile phase that was flowed at 1.0 mL/min. The column temperature was set at 35 °C. A series of narrow polystyrene molecular weight standards (Polymer Laboratories) with molecular weight ranging from 30,000 to 500 Da were used to calibrate the GPC column set. Oligomeric separation of the 500 Da polystyrene standard was achieved because of high chromatographic resolution. A Waters 2410 refractive index detector was used to monitor the GPC eluent. The internal temperature of the refractive index detector was set at 35 °C.

Thermal Spray Device (GPC-MALDI-TOF MS Interface)

The automated GPC-MALDI MS employed an LC-Transform Series 500 interface (Lab Connections, Inc., Northborough, MA). This system was modified for a matrix co-deposition mechanism with GPC effluent and has been previously described [43]. Dithranol was used as the matrix and was prepared as 15 mg/mL in HPLC grade THF with the addition of 2% (vol/vol) saturated sodium nitrate in THF. The matrix solution flow rate was 0.2 mL/min and directed towards a Valco (Houston, TX) tee connector where mixing with GPC effluent occurred prior to deposition on the MALDI sample target. The nozzle temperature was set at 193 °C and the nitrogen sheath gas was adjusted to a pressure of 25 psi. While evaporating most of the solvent, the uniform micro-cocrystals between sample molecules and matrix were formed because of the well-controlled experimental conditions. After the GPC experiment, the MALDI target was subjected to MALDI-TOF MS analysis.

MALDI-TOF Mass Spectrometry

The MALDI-TOF MS data was obtained with an Applied Biosystems Voyager DE-STR TOF (Framingham, MA) mass spectrometer, operating in the reflector mode. Ions were formed by laser desorption at 337 nm (N_2 laser, 3 ns pulse width, 10^6 W/cm^2, 100 μm diameter spot), accelerated to 25 kV and detected as positive ions. During the ionization process a delay time of 100 to 175 ns was applied before acceleration. Additionally, the grid and guide wire voltages were set at 75.0 and 0.030% of the applied acceleration voltage, respectively, to focus the beam of ions. Typically, 256 laser shots were averaged for each spectrum.

GPC-ESI-TOF Mass Spectrometry

The solvent delivery system for on-line GPC ESI-TOF MS experiments used an Agilent (Palo Alto, CA) 1100 HPLC system. The GPC column set and all other GPC experimental conditions used were the same as described in the gel permeation chromatography section. The ESI-TOF MS data was obtained with an Applied Biosystems Mariner mass spectrometer equipped with a Turbo electrospray ion source (Applied Biosystems). The experimental set-up is somewhat similar to that described by Simonsick and Prokai [38]. The main difference between the two designs is the location where charge agent and GPC effluent mixing occurs. Specifically, in their set up the charge agent solution was coaxially sprayed with GPC effluent and thus mixing occurred at the end of the spray needle. For the experiment here, the charge agent solution and GPC effluent were mixed in a Valco Cross connector before the ESI source. The charge agent solution consisted of isopropanol (IPA) with 2% (vol/vol) of saturated sodium nitrate solution in IPA. A built-in syringe pump at a flow rate of 10 μl/min delivered the charge agent solution. The split ratio to the waste and to the ESI-MS was solely controlled and adjusted by the internal diameter and length of the waste line tubing. The total flow rate directed to the ESI MS instrument was determined to be approximately 150 μl/min. The spray tip

Table 1. Average molecular mass values and molecular weight distributions of the OH PDMS obtained from different analytical techniques

MW				
Analytical techniques	M_n	M_w	M_z	Polydispersity (M_w/M_n)
Conventional GPC	796	1112	2221	1.40
MALDI-TOF MS	751	844	945	1.12
ESI-TOF MS	635	672	722	1.06
GPC-MALDI-TOF MS by spectra-summing	1830	2909	3910	1.59
GPC-MALDI-TOF MS by recalibration	1063	1400	3311	1.32
GPC-ESI-TOF MS by spectra-summing	623	731	933	1.17
GPC-ESI-TOF MS by recalibration	641	867	1782	1.35

and nozzle potentials were set at 5000 and 100 volts, respectively. Positive ion mode was used for all ESI MS measurements.

Data Analysis

The molecular weights and molecular weight distributions of a polymer were calculated by the following formulae:

$$M_n = \Sigma\ (N_i * M_i)/\Sigma M_i \quad (1)$$

$$M_w = \Sigma\ (N_i * M_i^2)/\Sigma(N_i * M_i) \quad (2)$$

$$M_z = \Sigma\ (N_i * M_i^3)/\Sigma(N_i * M_i^2) \quad (3)$$

$$PD = M_w/M_n \quad (4)$$

where M_n, M_w, and M_z represent number-average, weight-average, and z-average molecular mass, respectively and where N_i is the number of polymer molecules at molecular mass M_i. PD is the polydispersity index or molecular weight distribution. These average mass values were determined from GRAMS 32 (Galactic Industries, Salem, NH) and Millennium 32 software (Waters Corporation).

Results and Discussion

Comparison of Average Mass Values by On-Line GPC-ESI and Automated GPC-MALDI-TOF MS Analysis

Average mass values for a relatively low molecular weight hydroxyl terminated PDMS (OH-PDMS) sample were obtained from traditional GPC that was calibrated with narrow polystyrene standards from direct ESI and MALDI MS analysis and from a summation of mass spectra of OH PDMS fractions also determined by both mass spectrometric methods. The determined average mass values are summarized in Table 1. From traditional GPC analysis the PD of the OH-PDMS polymer was determined to be 1.40, indicating a relatively broad molecular weight distribution.

It is well documented that direct MS analysis underestimates the MWD of polydispersed polymers. From our experiments the PD of the OH-PDMS sample evaluated by direct ESI and MALDI MS differs from traditional GPC by 24.3 and 20.0%, respectively. To approximate where in the MWD the MS method underestimates the oligomer population one can compare the first, second, and third order average mass values (M_n, M_w, and M_z, respectively) which are increasingly dependant on the higher mass oligomers within the MWD. For both direct ESI and MALDI MS the determined M_z average mass differs from GPC by 67.5 and 57.5% respectively. This indicates that direct ESI-TOF and MALDI-TOF MS analysis of this polymer significantly underestimates the higher mass oligomers within the molecular weight distribution.

Figure 1a and b illustrate the differential refractive index trace from GPC analysis and the total ion chromatogram (TIC) from on-line GPC-ESI MS analysis, respectively. The average masses in Table 1 for GPC-ESI MS were obtained by summing all the mass spectra from 11 to 16 min on the TIC (Figure 1a). Based on traditional GPC analysis this time frame should include the entire MWD for the sample. A PD of 1.17 was determined using the spectra-summing technique. This PD value is 16.4% lower than the traditional GPC analysis and is only marginally better than that obtained from direct ESI-TOF MS analysis. From the

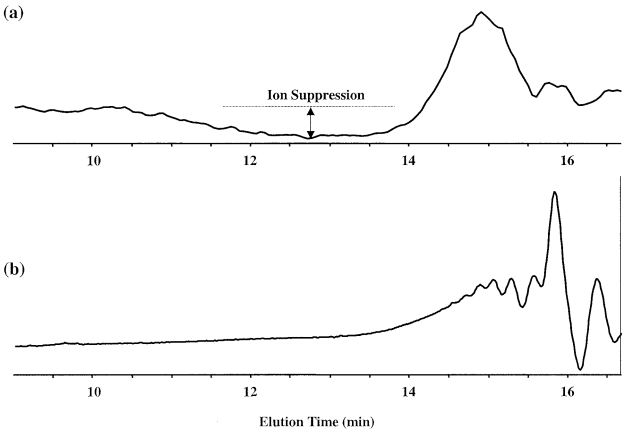

Figure 1. Total ion chromatogram (**a**) and dRI chromatogram (**b**) of the OH-PDMS sample in on-line GPC-ESI-TOF MS experiments.

relatively large difference of 58.0% in calculated M_z average mass compared to conventional GPC it seems that the GPC-ESI MS experiment still considerably underestimates the high molecular weight oligomers within the MWD for this polymer. The average masses in Table 1 for GPC-MALDI MS were obtained by summing spectra within the same time limits (11 to 16 min) as for the GPC-ESI-TOF MS experiment. A PD value of 1.59 was calculated from the GPC-MALDI-TOF MS data. Although this value has a relatively low difference of 13.6% compared to traditional GPC, the average mass values of M_n, M_w, and M_z are significantly higher than that calculated by traditional GPC. This indicates that GPC-MALDI-TOF MS effectively reports the high-mass polymers within the MWD, however the low-mass polymers are under-reported and it is proposed to be mainly due to the mass cutoff at 550 Da for the elimination of matrix interferences. Another possibility for this mass bias is that the low mass PDMS polymers have higher volatility than that of high mass PDMS polymers as suggested in a study by Yan et al. [9]. Under vacuum conditions in MALDI-TOF MS experiments, some of the low mass oligomers go into the gas phase as a result of evaporation without getting ionized through the normal MALDI process. This proposal may in fact be valid for dried droplet sample preparations where it is common to have heterogeneous mixing between matrix and oligomers. However, in this study the sample preparation is performed with a thermal spray deposition process where relatively homogeneous microcrystalline matrix and sample molecules are generated. Here, sample molecules are homogeneously embedded in the matrix [43, 50] and thus differences in volatility between the low and high mass oligomers should not be crucial.

There are several reasons for the differences in reported average mass values noted between GPC-ESI and GPC-MALDI-TOF MS analysis for this OH-PDMS polymer. The most fundamental of these reasons relates to the different underlying principles of operation (between ESI and MALDI) that govern ion transformation of PDMS polymer molecules into the gas phase. We also believe that these differences can in part be due to the differences in versatility between GPC-ESI and GPC-MALDI-TOF MS methods. GPC-MALDI is an off-line technique and as such the fractionated oligomers are isolated on the MALDI sample plate almost indefinitely. Even after several MALDI measurements, most of the fractionated polymer sample remains unconsumed. This makes it very convenient to optimize MALDI experimental parameters (grid voltage, delayed extraction etc.) so as to achieve optimal signal-to-noise (S/N) ratio of the oligomer peaks throughout the entire MWD. Also, with essentially unlimited analysis time it is possible to sum many scans for one particular GPC fraction. This can be especially beneficial for observing the less concentrated and less efficiently desorbed high mass polymers within the MWD.

With the inherent real time analysis of the on-line GPC-ESI-TOF MS there is very restricted amount of analysis time available and as such this limits the number of spectra that can be summed per sample analysis. The limited analysis time per mass spectrum makes it difficult to optimize ESI experimental conditions so that high mass polymers within the MWD can be observed. Also, it is unlikely that one constant optimal set of experimental conditions be applied for all the oligomers within a broad MWD. There are at least two analytical strategies that can be employed to compromise the experimental conditions for low and high mass polymers. First, ESI experimental parameters can be optimized from direct analysis of the non-fractionated polymer sample. However, this can be troublesome for optimization of the high mass polymers since these compounds in a polydisperse polymer sample are discriminated and perhaps not observed at all. Thus, optimization must occur on low to moderate mass polymers within the MWD, which according to the study here does not help to observe the high mass polymers within the MWD once GPC is applied. A second strategy would be to isolate a high mass fraction in a vial and optimize experimental parameters from direct analysis of this high mass fraction. However, this precludes the notion of high-throughput analysis of polymer samples for which we are attempting to develop a method.

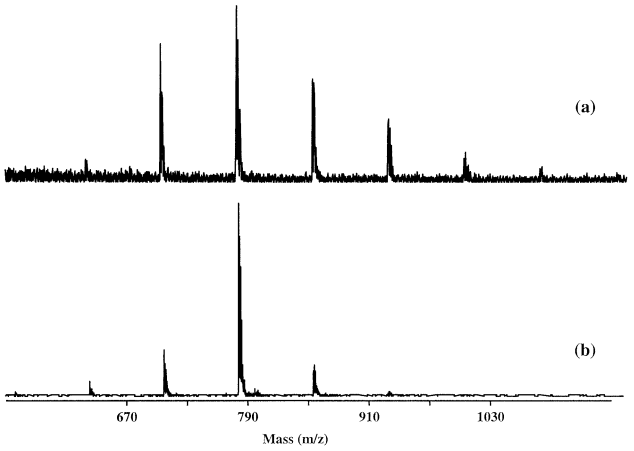

Figure 2. Typical mass spectra of PDMS samples at the same elution time from automatic GPC-MALDI-TOF MS experiment (**a**) and from on-line GPC-ESI-TOF MS experiment (**b**).

Evaluation of the Mass Spectra

For both hyphenated techniques the same GPC column set was used. Figure 2 illustrates mass spectra from the same elution time analyzed by GPC-ESI and GPC-MALDI-TOF MS methods. In both Figure 2a and b the decamer is the most intense oligomer observed. This confirms that the GPC in both hyphenated techniques have similar size exclusion properties. However, there are seven oligomers observed the GPC-MALDI experiment (Figure 2a) and five oligomers observed in the GPC-ESI experiment (Figure 2b). Moreover, in the GPC

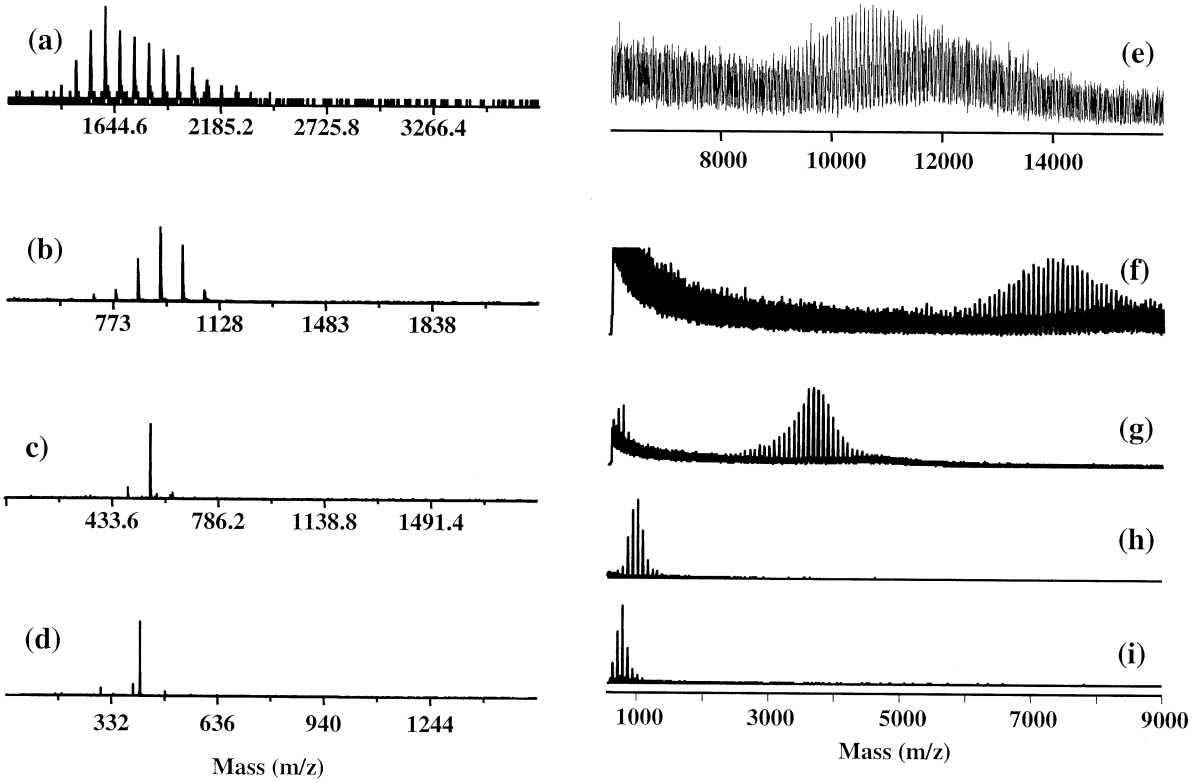

Figure 3. Overlaid mass spectra of the OH-PDMS obtained from both hyphenated techniques. Traces from (**a**) to (**d**) represent the mass spectra eluted sequentially at 13.5, 14.7, 15.0, and 15.3 min from on-line GPC-ESI-TOF MS experiments. Traces from (**e**) to (**i**) represent the mass spectra sequentially eluted at 10.5, 11.0, 12.4, 14.0, and 14.6 min from automatic GPC-MALDI-TOF MS experiments.

ESI experiment the ratio of intensities between the adjacent oligomers and the decamer is less than 25%. Comparatively, this ratio is approximately 80% in the GPC-MALDI experiment. The lower chromatographic resolution in the GPC-MALDI experiment can be explained by the potential mixing of oligomers that can occur sometime during the thermal-sprayed deposition process.

Figure 3(a–d) and 3(e–i) illustrate mass spectra at different elution times for the GPC-ESI and GPC-MALDI-TOF MS experiments, respectively. Very narrow polydispersed polymer fractions were obtained in each spectrum as a result of GPC fractionation. Performance of the GPC-ESI MS analysis was very efficient in the low molecular weight range (<2000 Da). In fact Figure 3c and d indicate truly mono-disperse fractions as they contain single OH-PDMS oligomers in the low molecular weight range; namely the sodiated pentamer and heptamer, respectively. Observation of these single oligomers indicates the efficient GPC column set employed and confirms that the on-line GPC-ESI MS interface set-up has extremely low dead volume. Much lower ion intensities are observed in the higher mass region (>2000 Da) and the highest molecular mass observed is under 4000 Da. GPC-MALDI-TOF MS analysis of the same polymer resulted in mass spectra with excellent S/N ratio in the higher mass region as illustrated in Figure 3(e–g). The highest oligomeric mass observed was approximately 12,000 Da (Figure 3e). Overlapping matrix peaks compromised the quality of mass spectra below 600 Da and no certainty could be given to the observation of oligomer peaks below 550 Da. The major difference between these techniques for the analysis of this OH-PDMS polymer sample is that GPC-ESI MS effectively reports the low-mass oligomers and underestimates the high-mass oligomers, while GPC-MALDI MS effectively reports the high-mass oligomers and underestimates the low-mass oligomers.

Regarding discrimination of the high mass polymers by GPC-ESI MS, an interesting observation can be noted in the TIC (Figure 2a) for this experiment. The recorded total ion current decreases below that of the mobile phase within the retention time frame (11–14 min) where high mass oligomers are known to elute, according to the GPC-MALDI MS data (Figure 3e–i). This ion current suppression is not believed to be an instrumental anomaly as it has been repeatedly observed in iterated OH-PDMS sample runs. The ion suppression observed indicates a difference in ion desorption efficiency of the high mass relative to the low mass oligomers (14–16 min) for which a positive ion current relative to baseline is observed. Several experimental factors including added co-solvents and charge agent, drying gas rate, needle position, and all applied voltages within the ESI source need to be considered for detection of the high mass oligomers within the MWD.

Table 2. Total ion intensity of three poly (dimethyl siloxane) samples obtained from on-line GPC-ESI MS experiments

Samples	OH-PDMS	HB-PDMS	ME-PDMS
Calculated relative total ion intensity compared to OH-PDMS	1100 Da nominal mass	1700 Da nominal mass	1200 Da nominal mass
Measured from TIC	100	76.4	69.5
From summed MS spectra	100	46.7	30.1

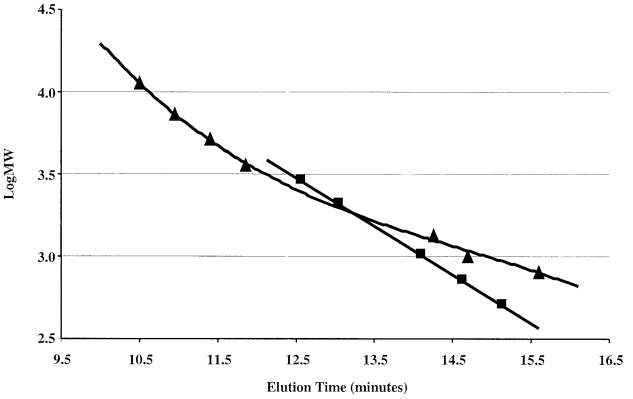

Figure 4. Calibration curves generated from automated GPC-MALDI-TOF MS (filled triangle) and on-line GPC-ESI-TOF MS (filled square).

Although we admit that some optimal combinations of experimental parameters may exist, we were not able to achieve such conditions to remedy the ion suppression that occurred with the high mass oligomers. We propose two possible explanations for this ion suppression phenomenon. First, this may be caused by differences in solubility between high and low mass polysiloxane polymers within desolvating droplets. In general, solubility of a polymer in solution decreases with increasing molecular mass of the polymer [51]. During the rapid desolvation process, the concentration of the polymer in ESI droplets increases dramatically. Perhaps the high mass polymers *precipitate out* from the partially desolvated droplet, thus precluding transfer to the gas phase. In contrast, the relatively low mass polysiloxane molecule has higher solubility in the desolvating droplet such that it undergoes transfer into the gas phase.

Secondly, it is known that the surface tension of a polymer solution is proportional to the molecular masses of the polymer [52]. We propose that surface tension in the electrospray droplets may play an important role in this observed mass bias. This aspect was discussed previously by Maziarz et al. [53] for ESI-MS analysis of polymer blends. In the current study the mass bias is observed purely as a function of polymer molecular weight eluting from the GPC columns. The higher mass eluting polymers result in a relatively high surface tension that may suppress ESI droplet formation. As the molecular mass of the eluting polymer decreases the surface tension of the ESI droplet decreases such that transfer of the PDMS into the gas phase becomes more favorable. We concede that these two proposals may only partially explain the observed phenomenon. In fact, recent mechanistic studies by Zhou and Cook [54] on the dynamics of the ESI desolvation process may provide further understanding of the underlying principles that cause the ion suppression observed in this study.

Interestingly, we observed differences in ion suppression between the PDMS samples that differed in end group chemistry under constant experimental conditions. Table 2 summarizes the relative signal intensities determined from the TIC and summed mass spectra for each of the three PDMS samples evaluated under constant experimental conditions. This data may suggest that ion desorption efficiency in GPC-ESI-TOF MS experiments for PDMS samples is somewhat dependent on the polarity of the end group chemistry [53]. A more exhaustive study to evaluate this notion is the topic of future research. Comparatively these same PDMS samples analyzed by GPC-MALDI-TOF MS did not show any difference in signal intensity.

Recalibration of GPC Using Mass Data

The GPC calibration curve was regenerated from mass values of selected GPC fractions from both hyphenated techniques. Several research groups have also used this method to obtain absolute mass values [10, 11, 39, 40, 42]. The regenerated calibration curves from the two experiments are illustrated in Figure 4. Linear correlation ($R^2 = 0.9997$) is obtained in the low mass region by GPC-ESI-TOF MS. It should be noted that there was no data from the high-mass fractions (>4000 Da) available for recalibration. Linear correlation was observed in the higher mass region for GPC-MALDI-TOF MS, however over the broad molecular weight range a third-order polynomial curve fit ($R^2 = 0.9981$) was used to construct the calibration curve. The non-linear behavior can be explained by the deviation between hydrodynamic volume and molecular weight over a broad molecular weight range in the GPC size exclusion process. The M_n and M_z values calculated from the recalibrated curve from GPC-ESI-TOF MS experiment (Figure 4) were determined to be approximately 19% lower than that obtained from traditional GPC. The M_n and M_z values calculated from the recalibrated method in the GPC-MALDI-TOF MS experiment were determined to be 33.5 and 49.1% higher than that from traditional GPC, respectively. The differences of PD calculated by GPC-MALDI and GPC-ESI-TOF MS from that of traditional GPC were determined to be 5.71 and 3.57%, respectively (Table 1).

These results demonstrate that GPC-MALDI-TOF MS can be a useful internal calibration device for a GPC column set over a broad molecular weight range. GPC-ESI-TOF MS covers only a very narrow portion of the MWD, however it is ideal for calibrating the lowest

mass portion of the MWD that is sometimes not obtained by MALDI-TOF MS analysis due to chemical noise associated with matrix peaks.

Conclusions

Both on-line GPC-ESI and automatic GPC-MALDI-TOF MS can be very useful for characterization of polymer samples. GPC-MALDI-TOF MS experiments were performed in a completely automated but off-line manner and provided detailed information on the high-mass polymers within MWD of the PDMS samples evaluated here. However, the information of the polymers on the lower mass (<550 Da) is completely masked due to the matrix interference. By contrast, GPC-ESI-TOF MS experiments were performed in a true on-line manner. Superior chromatographic resolution was achieved in the low molecular weight range based on the observation of truly mono-disperse PDMS oligomers. The analysis of the higher mass fractions (>4000 Da) was somewhat unsatisfactory due to *ion suppression*. From this work we anticipate that on-line GPC-ESI and automated GPC-MALDI-TOF MS have potential to be used as high-throughput characterization methods for PDMS materials.

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